THERMAL DESORPTION TREATABILITY STUDIES: REMOVING CHLORINATED ORGANIC COMPOUNDS FROM SOILS

Jerome P. Downey, ***Lawrence D. May***, and Kari D. Moore
Hazen Research, Inc., Golden, Colorado, USA

ABSTRACT: Hazen Research, Inc. has developed a bench-scale apparatus and methodology especially suited to thermal desorption treatability studies of media contaminated with chlorinated and recalcitrant compounds. A batch rotary kiln system is used to mix the media while maintaining it at relatively uniform temperature. Desorption characteristics of organic contaminants such as polychlorinated biphenyls (PCBs), dioxins, furans, petroleum-based organic compounds, and other volatile (VOC) and semivolatile (SVOC) organic compounds have been examined. Data show that most organic compounds can be desorbed from soils and sludges at temperatures ranging from 100 to 650°C and retention times of 5 to 30 minutes. Hazen's experience in performing thermal desorption studies on materials contaminated with chlorinated compounds is discussed. The experimental apparatus and methodology are disclosed, along with a discussion of the relationships between desorption efficiency and the pertinent process parameters.

INTRODUCTION

Technology. Thermal desorption technologies use direct or indirect heat to vaporize and remove organic compounds from soils, sludges, and other solid materials. Whereas incineration is intended to fully combust organic compounds, thermal desorption processes physically separate the contaminants from the media, while minimizing organic decomposition. Air or inert gas is normally used to convey the vaporized organic compounds from the contaminated media, but recycled process gas can also be used. Process gases containing vaporized organic compounds can be treated by a number of secondary treatment processes, including thermal oxidation, condensation, carbon adsorption, or chemical neutralization.

Objective. The main objective of most batch kiln thermal desorption test programs is to assess whether the cleanup criteria can be met; if so, the optimization of the process operating parameters becomes the focus of the test work. Cleanup standards for most sites are determined by the appropriate federal, state, or local regulations, or may even be determined on a site-by-site basis. Therefore, the cleanup goal may not be consistent from one site to the next. As a general guideline, the Universal Treatment Standard (40 CFR sec. 268.48) is often quoted.

Testing. Since 1992, Hazen has performed more than 40 studies on materials contaminated with various volatile and semivolatile organic compounds. These studies were conducted using representative samples of soils, sediments, and sludges from RCRA and CERCLA sites throughout the U.S. In many cases, the media tested contained more than a single contaminant.

THERMAL DESORPTION TESTING

Media and Contaminants. Soils and sludges are the most common media treated by thermal desorption technology. These often come from areas around historical chemical processing plants, drainage basins downstream of such plants, tailing ponds, and even from river dredgings. Contaminants can include inorganic species, organic species, and radionuclides. The organic compounds are classified as either volatile or semivolatile, depending on the boiling point. Generally, compounds that boil below 205°C are considered volatile while those that boil above 205°C are classified as semivolatile. Boiling points for the contaminants of concern are key information when considering the application of thermal desorption; Table 1 summarizes the boiling point ranges for common types of contaminants. Most troublesome organic compounds are amenable to thermal desorption in the range of 100 to 650°C. Some of the media tested, the contaminants of concern, and their concentrations in the untreated media are summarized in Table 2.

TABLE 1. Typical boiling point ranges for common contaminants.

Contaminant Category	Boiling Point Range, °C
VOCs	<205
SVOCs	>205
2,3,7,8 TCDD	500d
PCBs	275 - 385

TABLE 2. Contaminant concentrations in untreated media.

Media	Contaminant	mg/kg
Soil/sludge	Bis(2-chloroethyl)ether	6.04 - 6.56
Soil/sludge	1,2-Dichlorobenzene	0.38 - 0.42
Soil/sludge	1,2-Bis(2-chloroethoxy)ethane	15.2 - 15.8
Soil	Pentachlorophenol	27.5 - 46.4
Soil	Total dioxins	0.35 - 0.54
Soil	Total furans	0.023 - 0.040
Soil	PCBs, Aroclor 1248	6.3 - 26,300
Soil/humus	PCBs, Aroclor 1248	20,000
Soil/clay	PCBs, Aroclor 1248	800
Sludge	PCBs, Aroclor 1248	280,000 - 340,000
Sediment	PCBs, Aroclor 1248	260

Apparatus. A 4-inch-diameter batch quartz kiln system (Figure 1) is used for bench-scale thermal desorption testing. Operating temperatures up to 1,000°C are attainable by indirectly heating the kiln in an insulated clamshell furnace. Raised dimples act as lifters to enhance the mixing and tumbling of the sample as the kiln rotates. Typical sample charges range from 300 to 1,000 grams, depending on the material to be tested and the planned operating conditions. Control parameters include temperature, pressure, kiln rotational speed, sweep gas composition, and gas flow rate. Process exhaust gases can be treated using condensers, carbon columns, or a thermal oxidizer. Alternatively, the exhaust gases can pass through an emission sampling train to quantify volatile and semivolatile organics, including PCBs, dioxins, and furans. Additionally, a portion of the exhaust gas can be analyzed for concentrations of O_2, CO_2, CO, SO_2, NO_X, and THC using continuous emissions monitors (CEM).

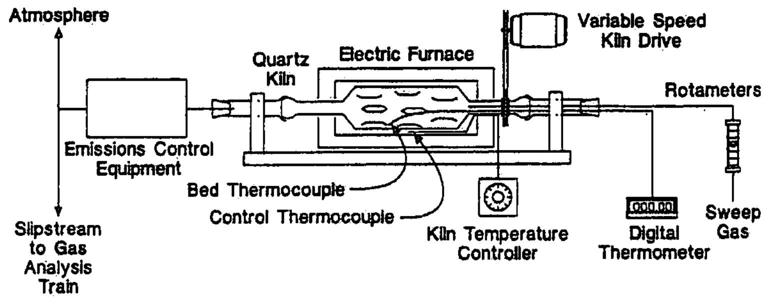

FIGURE 1. Batch rotary kiln system.

Methodology. For a typical thermal desorption test, a known mass of a contaminated soil or sludge is added to the kiln. The kiln is placed in the clamshell furnace and a thermocouple is positioned in the media to measure the temperature. Sweep gas (nitrogen or a blend of nitrogen and air) and the kiln rotation are started. In some tests, the time required for the media in the kiln to reach the designated temperature is defined as the retention time, at which point the heat is turned off and the kiln is removed from the furnace. In other applications, the media are maintained at the designated temperature for a set period of time. During a test, selected data such as temperatures and gas composition are continuously recorded by a data acquisition system. Data not electronically recorded (such as pressures and flow rates) are manually entered onto operational data sheets.

Following a test, the system is disassembled and the products recovered. The mass and/or volume of each product stream is quantified. General physical characteristics of each sample are recorded and chemical and physical analyses may be performed. Representative splits of the test products are packaged and saved for analyses according to the designated protocols for the specific program.

Advantages. The batch kiln system and test methodology offer distinct advantages over other practices. Only a small sample mass is needed to quantify the desorption characteristics of a contaminated soil or sludge. The actual temperature of the media is measured, providing more accurate information about the process requirements. The rotating kiln provides mixing not available in static applications, improving the potential for physically separating contaminants from the media. In addition, the potential for "clinkers" (agglomerates of material that become very hard on the outside and may not be sufficiently treated on the inside) to develop can be identified. On-line gas analysis can be performed and problems with plugging of the gas handling system can be seen. Finally, the methodology is economical; several tests can be run to assess organic removal as a function of time and temperature at a relatively low cost.

Quality Assurance. Several measures are employed to ensure that the data generated from a desorption test are consistently of high quality. The following protocols are followed:

- Representative portions of contaminated media and test products are analyzed according to recommended protocols (EPA SW-846).
- At least one replicate test is performed per program.
- Routine equipment calibration is conducted, including:
  - Verification of gauge, thermocouple, and flowmeter readings.
  - Confirmation of CEM measurements against certified span gas.
  - Verification of scale accuracy using calibrated weights.
- Equipment is precleaned and triple rinsed.
- Sample blanks are taken when emission sampling is performed.
- Analytical samples are collected and stored in precleaned amber glass jars with Teflon-lined lids, and refrigerated if appropriate.

For all tests, data are recorded both electronically and manually to document and verify the important parameters. In addition, a project journal is maintained to record aspects of a program not covered by routine data collection. All data and results are reviewed by senior members of Hazen's technical staff to ensure accuracy and completeness.

Results. Thermal desorption studies have been conducted with a variety of contaminant types and concentrations in many types of media. Some representative results are summarized in Table 3. Except where noted, retention time is defined as the period of time that the sample was held at the stated temperature.

The first three entries in Table 3 demonstrate the effectiveness of thermal desorption in removing organic compounds with relatively low boiling points, such as bis(2-chloroethyl)ether, 1,2-bis(2-chloroethoxy)ethane, and 1,2-dichlorobenzene. Nearly complete removal of each compound was achieved by processing the samples under relatively mild conditions, i.e., 10 minutes at 230°C.

The next three examples in Table 3 illustrate the effect of temperature on the removal of pentachlorophenol from samples of contaminated soil. Pentachlorophenol proved somewhat more difficult to remove, as relatively high concentrations of the compound remained with the solids after processing for 20 minutes at 340°C. Greater than 99% removal was obtained by processing the

TABLE 3. Summary of typical results for thermal desorption studies.

Number of Tests Summarized	Media	Time, min.	Temp., °C	Contaminant of Interest	Untreated, mg/kg	Treated, mg/kg	% Removal Efficiency
2	Soil/sludge	10	230	Bis(2-chloroethyl)ether	6.04 - 6.56	<0.011	99.81 - >99.99
				1,2-Dichlorobenzene	0.38 - 0.42	<0.043	88.68 - >99.99
				1,2-Bis(2-chloroethoxy)ethane	15.2 - 15.8	<0.014 - 0.036	99.76 - >99.99
3	Soil	10 - 30	340	Pentachlorophenol	27.5 - 46.4	0.99 - 1.39	96.40 - 97.00
3			455			<0.130	99.53 - >99.99
3			595			<0.130	99.53 - >99.99
3	Soil	10 - 30	340	Total dioxins	0.35 - 0.54	0.35	0.00 - 35.19
3			455			0.0007	99.80 - 99.87
3			595			0.0	>99.99
3	Soil	10 - 30	340	Total furans	0.023 - 0.040	0.006	73.91 - 85.00
3			455			0.0	>99.99
3			595			0.0	>99.99
1	Soil	GEC	540 - 595	PCBs, Aroclor 1248	26,300	<1	>99.99
5	Soil				6.3 - 120	<1	>99.99
2	Soil/humus				20,000	<1	>99.99
2	Soil/clay				800	<1	>99.99
2	Sludge				280,000 - 340,000	<1	>99.99
2	Sediment				260	<1	>99.99

Note: GEC - tests were run until gas evolution ceased.

material at 455°C; no measurable improvement was realized by increasing the temperature to 595°C.

The test series conducted with soil samples contaminated with dioxins and furans showed that greater than 99.99% removal of each compound was possible. As expected, the furans were more easily desorbed, and greater than 99.99% removal was achieved when the samples were processed at or above 455°C. For the dioxins, 595°C was required to exceed four nines removal efficiency.

In contrast to the other tests summarized in Table 3, the PCB-bearing media were typically processed at temperature until evidence of gas evolution had virtually ceased. This mode of operation was initially selected because the as-received samples had high initial moisture content and/or high levels of other, more volatile contaminants relative to the PCB concentrations (measured as Aroclor 1248). This methodology has proven exceptionally successful for PCB removal. Regardless of the media type or the initial PCB concentration, every sample that was processed within the temperature range of 540 to 595°C analyzed less than 1 mg/kg PCB.

Conclusions. The removal efficiency of any given contaminant will be affected by the type of matrix (sand, clay, soil, sludge, or sediment). A well-designed test program and experimental matrix are essential to determine the feasibility of applying thermal desorption technology. The batch kiln system and methodology can be used to establish the efficiency at which various organic compounds can be desorbed from a representative sample of media. Also, the requisite solids temperature and retention time can be expediently determined from batch kiln test results. However, it is important to understand the limitations of conducting small-scale tests in batch mode and the risks involved in extrapolating laboratory data to a commercial scale operation. Before implementing any thermal desorption process, it is advisable to conduct confirmatory tests in continuous mode using a larger, pilot scale system.

REFERENCES

Regulations for Implementing the Procedural Provisions of the National Environmental Policy Act. 40 CFR sec. 268.48.

U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. SW-846.